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Journal of Polymer Science, Part B

Polymer Letters

Editorial Board: R. M. Fuoss • J. J. Hermans • H. Mark • H. W. Melville • C. G. Overberger • G. Smets

Contents

ADI EISENBERG: An Idealized Multidimensional WLF Equation 273

H. K. HALL, JR. and J. W. BERGE: Aromatic Polyoxamides from Diphenylthiol Oxalate 277

ANTON PETERLIN: Thickening of Polymer Single Crystals during Annealing 279

J. C. MITCHELL: The Melting Point of *cis*-1,4-Polybutadiene 285

V. STANNETT and H. YASUDA: Liquid versus Vapor Permeation through Polymer Films 289

MINORU IMOTO, TAKAYUKI OTSU, and TOSHIO ITO: Radical Homopolymerization of 5-Cyanobicyclo [2.2.1]-hept-2-ene 295

HIDEHIKO KOBAYASHI: Evaluation of Viscosity Constants 299

HIDEO SAWADA: High Conversion Polymerization of Methyl Methacrylate 305

STUART M. ELLERSTEIN: A Glass Temperature Relationship 311

A. D. KETLEY: The Cationic Polymerization of 3-Methylbutene-1 and 1,1-Dimethylcyclopropane 313

JORGE HELLER and DONALD J. LYMAN: Measurement of Glass Transition Temperatures of Polymers by a Differential Pressure Transducer 317

W. RING: Remarks About Sequence Distribution Functions. Their Relation to Copolymer Crystallinities 323

YVES GALLOT, PAUL REMPP, and JAQUES PARROD: Anionic Grafting Reactions 329

continued inside

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Journal of Polymer Science **Part B: Polymer Letters**

Editorial Board:
R. M. Fuoss • J. J. Hermans • H. Mark • H. W. Melville • C. G. Overberger • G. Smets

Contents (continued), Volume 1, No. 6

HANS-GEORG ELIAS and URS GRUBER: Analyse von Copolymeren durch Trübungspunkt-Messung 337

F. R. DAMMONT: Synthesis of Poly-*m*-xylylene 339

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POLYMER LETTERS VOL. 1, PP. 273-276 (1963)

AN IDEALIZED MULTIDIMENSIONAL WLF EQUATION

The WLF equation (1), which was originally developed to correlate the mechanical or electrical relaxation times of glass-forming materials above the glass transition temperature, T_g, with those at a standard temperature (T_g or $T_s \approx T_g + 50$), has subsequently been modified to include the effects of pressure, or diluent, or tensile stress (2). The work of Fujita and Kishimoto (3) on polymer-diluent systems has shown that within a certain range of the variables involved, a time-temperature-diluent concentration superposition was possible; later work by McKinney, Belcher, and Marvin (4) on the dynamic compressibility of rubber and by O'Reilly (5) on dielectric relaxation of poly(vinyl acetate) has shown that time-temperature-pressure superposition was also possible. The last three papers offered a modified WLF equation to take into account the simultaneous variation of three parameters, i.e., time, temperature, and pressure or diluent concentration.

In this note, an idealized multi-dimensional version of the WLF equation will be presented, in which the effect on the relaxation times of a simultaneous variation in temperature, pressure, diluent concentration, and molecular weight is derived.

Since the WLF equation is based on the Doolittle equation (6) which expresses the viscosity of a liquid as a function of its free volume, a single expression for the free volume of a polymer as a function of the above variables will be presented first, and subsequently rearranged into the WLF form.

Effect of Pressure on Free Volume

As pointed out by McKinney, Belcher, and Marvin (4), this can be given as

$$f_{T,P} = f_g + \alpha_f(T - T_g) - \beta_f P \qquad (1)$$

where f is the free volume, T is the temperature, the subscript g is the glass transition, α_f is the free volume expansion coefficient, and β_f is the free volume compressibility. α_f equals approximately $\alpha_l - \alpha_g$ and $\beta_f \approx \beta_l - \beta_g$ where the subscripts l and g refer to the liquid and glass, respectively. If the effect of pressure alone is considered, it can easily be seen (2,5) that eq. (1) leads to a WLF equation in which $T - T_g$ has been replaced by $T - T_g - (\beta_f/\alpha_f)P$, which is equivalent to (2) $T - T_g - P(dT_g/dP)$ since $(\beta_f/\alpha_f) = (dT_g/dP)_f$.

Effect of Molecular Weight on Free Volume

Bueche (7) shows that

$$K'M = \alpha_f(T_g^{\infty} - T_g) \tag{2}$$

where M is the molecular weight, K′ is a constant, and the superscript ∞ denotes polymer of infinite molecular weight. This means that at the glass transition temperature of a polymer of finite molecular weight, the free volume contributed by the chain ends is just compensated by the free volume contraction as a result of cooling by $T_g^{\infty} - T_g$.

Since K′ is a constant, and plots of T_g versus 1/M yield straight lines in the high molecular weight range for all polymers investigated (8-10), eq. (2) can be rewritten as

$$K' = \alpha_f[dT_g/d(1/M)] \tag{2a}$$

and the fractional free volume contributed to the polymer as a result of lowering the molecular weight from infinity to M is

$$\Delta f_M = -(\alpha_f/M)[dT_g/d(1/M)] \tag{3}$$

Effect of Added Diluent on Free Volume

The effect of added diluent can be treated in a very similar manner, which is essentially identical to that employed by Ferry and Stratton (2) and by Fujita and Kishimoto (3) although it is somewhat different in appearance. In analogy with eq. (2), we can say that

$$K'' C = \alpha_f(T_{g_{c=0}} - T_g) \tag{4}$$

where C is the diluent concentration, and $T_{g_{c=0}}$ is the T_g of the pure polymer. Since plots of T_g versus C are linear at low concentrations of diluent (11), we can rewrite this equation as

$$K'' = \alpha_f(dT_g/dC) \tag{4a}$$

where K″ equals β of ref. 3), and obtain for the fractional free volume contributed to the polymer by the addition of diluent

$$\Delta f_c = -\alpha_f C (dT_g/dC) \tag{5}$$

assuming, of course that α_f does not change upon addition of small amounts of diluent and that (dT_g/dC) and α_f are independent of M.

The Multidimensional WLF Equation

To obtain the effect on the free volume upon simultaneous variation of temperature, pressure, diluent concentration, and molecular weight, a simple addition of eq. (1), (3), and (5) is, a priori, not enough since we are dealing with a two-component system, i.e., polymer and diluent; we must therefore either take into account the differences in the β_f and α_f values of these two materials in the presence of each other, which is very difficult, or assume that α_f and β_f do not change appreciably with composition (at low diluent concentration) or pressure.

The first of these assumptions seems reasonable in view of the finding of Simha and Boyer (12) that $(\alpha_l - \alpha_g)T_g$ is approximately constant; it should also be recalled that T_g does not vary greatly by addition of small quantities of diluent (3 to 8° per 1% diluent).

The effect on compressibilities seems much more difficult to estimate in view of the absence of data on polymer-diluent systems; for pure polymers α_f and β_f do seem to vary slightly with pressure. If, however, we confine ourselves to that pressure region in which these variations are small, and to low diluent concentrations, then we can add eq. (1), (3), and (5) to obtain

$$f_{T,P,M,C} = f_g + \alpha_f(T - T_g) - \beta_f P - (\alpha_f/M)[dT_g/d(1/M)] - \alpha_f C(dT_g/dC) \quad (6)$$

Substituting this expression into the Doolittle equation of the form

$$\ln a = B(1/f - 1/f_g) \quad (7)$$

(where a is the ratio of relaxation times) and developing it in analogy to the original WLF equation, we obtain, after setting $\beta_f/\alpha_f = dT_g/dP$

$$\log a_{T,P,M,C} = -17.4\{T - T_g - P(dT_g/dP) - (1/M)[dT_g/d(1/M)] + C(dT_g/dC)\}/[52 + T - T_g - P(dT_g/dP) - (1/M)[dT_g/d(1/M)] + C(dT_g/dC)\} \quad (8)$$

where 17.4 and 52 are the constants of the original WLF equation [$f_g/\alpha_f \approx 52$ and $B/2.303\, f_g \approx 17.4$]. Equation (8) may be written in a simplified form as

$$\log a_{T,P,M,C} = -17.4\,[T - T_g - \sum_i X_i(dT_g/dX_i)]/[52 + T - T_g - \sum_i X_i(dT_g/dX_i)] \quad (9)$$

where X represents P, (1/M), or C, depending on which variables are involved. This equation implies the existence of a general time-T-P-C-(1/M) superposition within a certain range of the parameters involved, and work on determining this range is now in progress.

It should be stressed that this equation is expected to hold only at relatively low diluent concentrations, at low pressures, and only in that range of the relaxation spectrum in which the relaxation times depend on the molecular weight only through its influence on the free volume; this immediately excludes the terminal regions since above a certain critical molecular weight those vary as $M^{3.4}$.

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AROMATIC POLYOXAMIDES FROM DIPHENYLTHIOL OXALATE

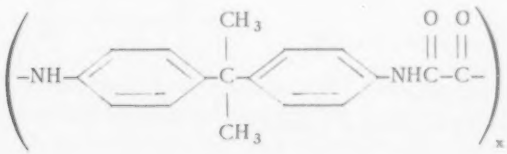
We have prepared film-forming aromatic polyoxamides for the first time by the reaction of aromatic diamines with the reactive ester diphenylthiol oxalate. The reactions of this ester with 2,2-di-(4-aminophenyl)-propane, 3,3′-diaminodiphenyl sulfone, 4,4′-diaminodiphenyl sulfone, 4,4′-diaminodiphenylmethane, and 3,3′-dimethyl-4,4′-diaminodiphenylmethane were carried out in tetramethylene sulfone solution. Polymerization occurred readily at 130-200°C. Polymer I was obtained reproducibly with inherent viscosity 0.4-0.5, polymer melt temperature > 400°C. It contained 1.05% sulfur, corresponding to a number average molecular weight of 6100, assuming two sulfur atoms per chain. The inherent viscosity could be raised 0.1-0.2 units by heating the powdered polymer under vacuum. Polymer II was obtained in lower molecular weight (η_{inh} 0.20), probably because the polar sulfone group decreases the reactivity of the amine ends. Two copolymers were also prepared (Table I).

TABLE I

Aromatic Polyoxamides

Parent diamine(s)	Polymer melt temperature	Inherent viscosity
2,2-Di-(4-aminophenyl)propane	> 400°	0.60 (NMP[a], 130°C.)
3,3′-Diaminodiphenyl sulfone	376°	0.20 (NMP, 130°C.)
75% 2,2-Di-(4-aminophenyl)propane 25% 4,4′-Diaminodiphenylmethane	> 400°	0.40 (NMP, 130°C.)
90%,2,2-Di-(4-aminophenyl)propane 10% 3,3′-Dimethyl-4,4′-diaminodiphenylmethane	> 400°	0.30 (NMP, 130°C.)
4,4-Diaminodiphenyl sulfone	> 400°	0.17 (H_2SO_4, 25°C.)

[a]N-methylpyrrolidone.



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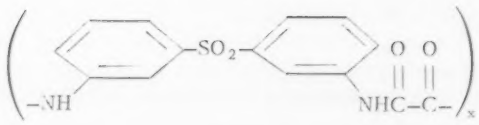

II

Sparkling clear, tough, flexible films were cast at 100°C. from dichloroacetic acid, N-methylpyrrolidone and N-acetylpyrrolidine solutions of polymer I, particularly the first. Clear tough films of polymer II were cast from solutions in tetramethylurea and other amide solvents.

A typical experiment was as follows: A 25-ml. conical three-necked flask was fitted with a motor-driven stirrer and a nitrogen bleed. In it were placed 1.9949 g. of powdered 2,2-di-(4-aminophenyl)propane, 2.4182 g. of powdered diphenylthiol oxalate, and 12.00 ml. of tetramethylene sulfone. Stirring was begun, nitrogen was passed in, and an oil bath maintained at 45°C. was raised to surround the flask. In 9 min. the ingredients dissolved and the solution was perfectly clear and homogeneous. After 10 min. more at 45°C. the solution became turbid and after another 10 min. became too thick to stir. The flask and fittings were then transferred to a 160°C. bath and held there for 24 hr. The flask was cooled and the contents were transferred to excess methanol in a Waring Blendor. After blending, the white fibrous polymer was filtered and reblended with methanol, filtered, and dried. The yield was 2.47 g. (100%), polymer melt temperature > 400°C., inherent viscosity 0.40 in N-methylpyrrolidone at 130°C. Heating the dried polymer at 250°C. and 1 mm. overnight raised the inherent viscosity to 0.60.

Diphenylthiol oxalate was prepared from thiophenol and oxalyl chloride (1) and recrystallized from glacial acetic acid, m.p. 120.0-121.8°C. (ref. (1) m.p. 119-120°C.).

We are deeply indebted to Mrs. Nancy G. Abbadini for excellent technical assistance and to Dr. F. B. Cramer for the 2,2-di-(4-aminophenyl)-propane.

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THICKENING OF POLYMER SINGLE CRYSTALS DURING ANNEALING

During annealing at constant temperature T close enough to the melting point the thickness L of polyethylene crystals steadily increases (1-6). The rate of thickening is faster at higher T. At constant temperature it rapidly decreases with time. According to Fischer and Schmidt (6), experimental data may be well represented by (Fig. 1).

$$L = L^* (1 + B \ln t) = L^* (1 + 2.303\ B \log t) \qquad (1)$$

The slope L*B rapidly increases with T and seems to be identical for single crystals precipitated from dilute solution and for samples isothermally crystallized from melt (Fig. 2).

Equation 1, leading to meaningless results when extended to t = 0, merely represents the asymptotic behavior of long period at large times. A reasonable relationship valid for any time reads

$$L = L^* [1 + B \ln (t + C)] = L^* [1 + 2.303\ B \log (t + C)] \qquad (2)$$

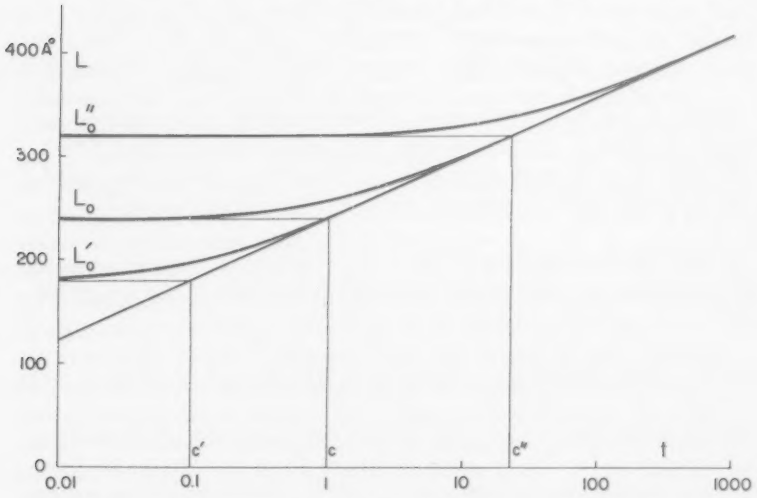

Fig. 1. Crystal thickness L as a function of t according to the asymptotic (eq. 1) and general (eq. 2) relationship for different starting lengths: $L_0' < L^*$, $L_0 = L^*$, $L_0'' > L^*$ with corresponding C', C, C''. The data L* = 240 A., L*B = 59 A. correspond to polyethylene single crystal annealing at 130°C.

The length L_0^* of the crystals at t = 0 equals L^* (1 + B ln C). The constant C follows from L_0 and L^* as ln C = $(L_0/L^* - 1)/B$. In the L, log t plots in Figure 1 the curves for L start at L_0 with a horizontal tangent, begin to increase slightly below t = C, reach the value L_0^* (1 + 0.693 B) at t = C, and then rapidly approach the asymptote. If L_0 is markedly below L^* the constant C turns out to be so small that before observation of long period can start the transition to the asymptotic behavior is already completed. The crystal thickening starts at an exceedingly high rate. If, however, L_0 is much larger than L^*, the large value of C results for a rather long while in a nearly constant thickness which only starts to increase very slowly when t approaches C.

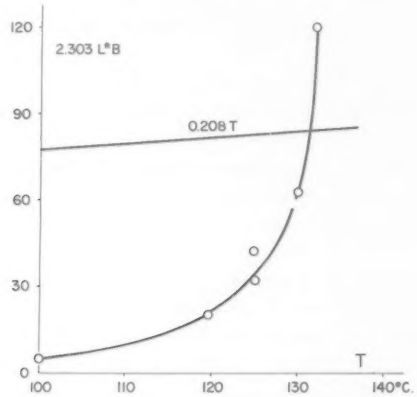

Fig. 2. Coefficient L*B from eq. (1) as a function of temperature according to Fischer and Schmidt (6). The broken lines represent L*B according to eq. (6) with Hoffman's data for σ^2/σ_e. Hirai's data yield a straight line which is situated too high to be included in the plot.

In order to check how well different mechanisms of long period growth may reproduce the observations, it is of some benefit to use the growth rate

$$dL/dt = L^*B \exp[-(L/L^* - 1)/B] = A \exp(-L/L^*B) \qquad (3)$$

instead of its integral L(t). The coefficient A contains all the factors independent on L. The decisive feature of the growth rate is the exponential function with the argument $-L/L^*B$. Two independent processes at crystal thickening may provide such a factor: surface nucleation (a) and collective mass transport (b) by jumps of the whole straight section between the (001) surfaces.

(a) According to Hirai et al. (5) the free energy increase for formation of a crystal nucleus of lateral dimension x (side length for a quadratic,

diameter for a circular cross-section) which is by one repeat unit d_0 = 2.52 A. thicker than the original crystal equals

$$\Delta F = \alpha x d_0 \sigma - \beta x^2 \sigma_e / L \qquad (4)$$

where α and β are shape parameters (4 and 1 for a quadratic, π and $\pi/4$ for a circular cross-section), σ and σ_e surface energy density at lateral and fold surfaces respectively. The maximum free energy increase $\Delta F^* = \alpha^2 d_0 \sigma^2 L / 2\beta\sigma_e$ for the critical nucleus characterized by $\partial\Delta F/\partial x = 0$ just represents the activation energy for surface nucleation by which the crystal increases its thickness. If the nucleation process is the slowest step in long period growth, the thickening rate reads

$$dL/dt = A \exp(-\Delta F^*/kT) \qquad (5)$$

which from comparison with eq. 3 yields

$$L^*B = 2\beta\sigma_e kT / \alpha^2 \sigma^2 d_0 \qquad (6)$$

for the growth rate coefficient.

With Hirai's values $\sigma_e = 67$, $\sigma = 7$ erg/cm.^{2}, $\alpha = 4\beta = 4$ one finds $2.303\, L^*B = 0.86T$ (in A.U.), i.e., 348 A. at T = 130°C. With $\sigma_e = 49$, $\sigma = 12.2$ erg/cm.^{2}, suggested by Hoffman and Weeks (7), the slope turns out to be 0.208T, i.e., 83.6 A. at 130°C. The latter values are plotted in Figure 2. Although they display the correct order of magnitude, they completely fail to reproduce the observed temperature dependence.

(b) When the crystal thickness increases, a substantial mass transport is required within every macromolecule by which the length of all the straight sections between consecutive folds is increased and their number proportionately reduced. The mass transport very nearly exclusively starts from both ends of the macromolecule. Two mechanisms may be considered: individual translation of Reneker-type dislocations (8) containing one excess CH_2 group and collective jumps of the whole straight section of the polymer chain between the (001) surfaces.

The probability for a displacement by $d_0/2$ along the chain axis of one excess CH_2 group by a single jump is proportional to $\exp(-E_d/kT)$ with E_d the activation energy for the longitudinal diffusion of the dislocation. The number n_j of individual jumps per macromolecule necessary for a thickness increase by d_0 is proportional to L^{-2} in the case of random diffusion and to L^{-1} for the more unlikely unidirectional motion. Another factor entering the growth rate is the probability of dislocation formation at the free ends of the macromolecule which is obviously independent on L. Altogether the consideration of mass transport by single jumps of Reneker type dislocations results in a coefficient A in the growth rate proportional to L^2 or L^1 which has to be combined with the

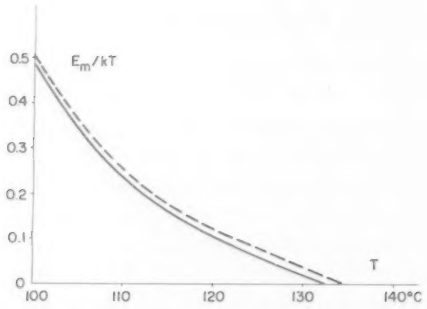

Fig. 3. Temperature dependence of E_m according to eq. (9) with (full line) and without (broken line) inclusion of the nucleation factor.

activation energy factor for surface nucleus formation (eq. 5) in order to obtain the growth rate in the form postulated by experiments (eq. 3).

The mass transport may be also achieved by a series of simultaneous jumps by d_0 of the whole straight section of the chain between the (001) surfaces. Such a jump is a collective phenomenon favored by the high covalence bonding forces in the chain direction which are nearly as strong as in a diamond lattice and the very much smaller lateral forces between adjacent chains. If the energy barrier between consecutive equilibrium positions of the monomer is E_m, the activation energy for such a collective jump is LE_m/d_0. The number n_L of such jumps per macromolecule needed for a thickness increase by d_0 and the frequency ν_L of longitudinal oscillation of the straight section of the chain are entering the thickening rate in the same way as above in the case of individual jumps of the dislocation. Again both factors are so slowly varying functions of L (L^3 for random diffusion, L^2 for unidirectional motion) that compared with the exponential function one may consider them as constant. Including also the activation energy for critical nucleus formation, one obtains for the thickening rate

$$dL/dt = A \exp(-LE_m/d_0\,kT - \alpha^2 d_0\sigma^2 L/2\beta\sigma_e kT) \qquad (7)$$

and for L*B

$$L^*B = kT/(E_m/d_0 + \alpha^2 d_0\sigma^2/2\beta\sigma_e) \qquad (8)$$

Because E_m rapidly decreases with increasing temperature as a consequence of lattice expansion in the a and b direction and of the smearing out effect of the incoherent longitudinal and rotational vibration of adjacent chains, L*B according to eq. (8) increases much faster than linearly with T in good qualitative agreement with experimental data (Fig.

2). One may even derive E_m from observed L*B values

$$E_m = (kT/L^*B - a^2 d_0 \sigma^2 / 2\beta\sigma_e)\, d_0 \qquad (9)$$

The main uncertainty is with σ^2/σ_e which is 0.73 erg/cm.^{2} according to Hirai (5) and 3.04 according to Hoffman and Weeks (7). With Hirai's data one obtains a temperature dependence of E_m (Fig. 3) which is very similar to the calculated values of energy barrier for rotational chain vibrations (9).

One may even go a step further and completely neglect the nucleation process for crystal thickening. In this extreme case the activation energy E_m equals kT/L*B. The corresponding curve plotted in Figure 3 only slightly differs from that according to eq. (9). Particularly in the former case E_m does not vanish below the melting point. The complete omission of the factor due to nucleation kinetics is certainly an oversimplification. But very likely also the simple calculation of the activation energy for stable nucleus formation according to eq. (4) has to be markedly modified in order to include the energy contribution of new lateral surfaces which appear as a consequence of hole formation during annealing of single crystals. Very likely the nucleus formation has to start at some large lattice defect, for instance at an interstitial fold plane with markedly enhanced lateral surface because only then the energy increase needed for critical nucleus formation is sufficiently low.

In comparing eqs. (5) and (7) with eq. (3) one must not forget that the values of the numerical coefficients are to a certain degree influenced by the dependence of A on L which was completely neglected in the present treatment. With increasing powers of L occurring in A the ordinate intercept L* and also the slope L*B in L(t) are slightly shifted to higher values. A more detailed investigation is under way and will be presented soon.

The discussion of the two cases presented leads to the impression that the temperature dependence of polyethylene crystal thickening during isothermal annealing may be better described by the mechanism of collective jumps of all the atoms in one straight chain section between the (001) surfaces than by that of individual jumps of Reneker type dislocations. This does not mean that one mechanism must be completely excluded but merely that it contribute much less to the thickness growth than the other one.

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THE MELTING POINT OF CIS-1,4-POLYBUTADIENE

Melting point values for cis-1,4-polybutadiene thus far reported in the literature have not exceeded +1°C. (1-11). Varying values have been reported, both because of sample variations (differing amounts and distributions of chain imperfections) and because of variations in experimental techniques used to measure the melting point (in particular, varying heating rates). Some workers have extrapolated their data to predict that the melting point of a perfectly regular (100% cis) cis-1,4-polybutadiene (T_m°) would be close to +1°C. (8,9). These extrapolations have been used to arrive at heats of fusion for the polymer from Flory's theory for melting point depression due to copolymeric impurities (12). One such value has been used in another investigation to estimate extents of crystallization from thermodynamic data (13).

We wish to report observation of melting points several degrees higher than the assumed T_m° value of +1°C. Our experiments show that these higher values are not due to orientation effects.

It is well known that the observation of polymer melting points approaching values corresponding to the melting of perfect macroscopic crystals requires extremely slow rates of heating (14). Values so obtained are desirable because they reflect chain properties uncomplicated by morphology effects (i.e., strain and surface energies) and should therefore be independent of prior treatment of the polymer. We have obtained melting points for a variety of cis-1,4-polybutadiene samples using standard volume dilatometric techniques. Several heating schedules were employed to show the magnitude of the effect of heating rate. The data are shown in Table I. Melting points obtained at the slowest heating rates are underlined to emphasize their greater significance.

Estimates of % cis-1,4 addition were obtained by infrared spectroscopy using a slight modification of the method of Silas, Yates, and Thornton (15). The melting point, T_m, was taken as the intersection of the volume-temperature curve of the melting sample with the reversible essentially linear expansion curve found for the molten polymer (the liquidus curve). The heating schedules were as follows:

A, A′: A specified temperature increase per day attained in 12-16 small adjustments of the bath temperature controller over 8 hr., followed by constant temperature overnight. A: −18° to −12°C., 6°/day; −12° to −8°C., 4°/day; −8° to −4°C., 2°/day; −4° to +11°C., 1°/day. A′: −26° to −17°C., 9°/day; −17° to 12°C., 5°/day; −12° to −6°C., 2°/day; −6° to +11°C., 1°/day.

B: A 1° increase in bath temperature control point every 8 min., temperature rise of 1° occurring in about 5 min. after each adjustment.

TABLE I

Melting Points of cis-1,4-Polybutadiene

Sample	cis-1,4-Addition, %	T_m, °C.	Heating schedule (rate near T_m)
I	96 ± 2	+5.2	A (1°C./day)
		–4.1	B (1°C./8 min.)
		–6.1	C (1°C./min.)
II	97.0	+6.2	A (1°C./day)
		–0.7	B (1°C./8 min.)
III	97.7	+6.3	A (1°C./day)
		–0.7	B (1°C./8 min.)
IV	96.9	+5.2	D (1.2°C./day)
IV–M	96.9	+5.2	D (1.2°C./day)
IV–MD	96.9	+5.2	D (1.2°C./day)
V	94.0	–0.8	A′ (1°C./day)
		–2.5	E (2°C./day)
		–7.2	B (1°C./8 min.)
VI	94.4	–0.8	A′ (1°C./day)
		–3.0	E (2°C./day)
		–7.3	B (1°C./8 min.)

C: A smooth rise in temperature at an average rate of 1°/min. brought about by heating the bath at a fixed wattage.

D: A smooth temperature rise brought about continuously over the 24 hour day by a clock motor drive on the bath temperature controller. –16° to –5°C., 4.4°/day; –5° to +12°C., 1.2°/day.

E: Advancement of the bath temperature control point by two degrees in a single adjustment each morning. The two degree rise was attained in about 15 min. and the temperature was held constant for the remainder of the 24 hour day.

Heating schedules, A, A′, and D, in which the temperature was raised very slowly and relatively smoothly were seen to yield the highest melting points. Schedule E, which may appear adequately slow if reported as 2°/day without further details, yielded somewhat lower T_m values.

An interesting phenomenon was observed in the experiments using heating schedules A and A′. Up to about 5 or 6° below the melting points, recrystallization was observed as an increase in density during the constant temperature overnight periods. Above this point, however, while no density change was observed overnight, the volume-temperature curves started at a lower slope in the mornings than they had shown in the preceding afternoons, i.e., the rate of melting with increasing temperature had been diminished by the constant temperature overnight periods. Apparently, then near the melting point we have observed an increase in stability of the crystalline structure without a measurable density change.

The experiments with samples IV, IV–M, and IV–MD show that orientation has probably not been a factor in these experiments. While none of the samples measured shows orientation observable as birefringence, high shearing in laboratory rubber mills has resulted in markedly altered crystallization kinetics in some of them. These effects can be eliminated by dissolving the milled samples and removing the solvent by evaporation. IV is a sample as received, IV–M is a milled portion of the same material, showing the crystallization kinetics effect, and IV–MD is a portion of the milled sample which has been recovered from solution, eliminating the crystallization kinetics effect. The fact that all three of these samples showed the same melting point (+5.2°C.) (and, indeed, identical volume-temperature curves) indicates that the shearing effect is of no consequence in our melting point experiments.

In the absence of additional data on the distribution of the non-cis-1,4 structural units in the samples studied, one cannot extrapolate the present data with confidence to 100% cis-1,4 addition to obtain the melting point, $T_m°$, of the structurally pure polymer. If the samples showing melting points around +5 or +6°C. have their structural imperfections closely grouped, leaving long uninterrupted sequences of cis-1,4 addition, the observed melting point values may be close to $T_m°$. If, on the other hand, one assumes a random distribution of the imperfections, the melting point-structural purity data plotted in accordance with Flory's equation (12) leads to a prediction of +11.5°C. for $T_m°$.

The present data are not very suitable for predicting the heat of fusion of cis-1,4-polybutadiene because the samples studied are not adequately characterized as to their distributions of structural imperfections. On the other hand, data extrapolating to $T_m° = +1°C.$ must also be regarded with caution.

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LIQUID VERSUS VAPOR PERMEATION THROUGH POLYMER FILMS

In a previous communication (1) it was shown that the permeability constants of methyl alcohol and water vapor in polyethylene were the same as those obtained with the corresponding liquid penetrants. The same was subsequently shown (2) to be true with water in a number of other polymers. However, with these systems the permeability constant is independent of vapor pressure and a simple check of liquid versus vapor behavior is possible. With most organic vapors, however, the permeability increases rapidly with increasing vapor pressure (3), and it has recently been reported (4,5), that with these systems the permeability to liquid penetrant is considerably greater than with the corresponding saturated vapor.

The rate determining process in permeation is normally the stepwise diffusion process through the film under the concentration gradient. Since the activities are identical, the concentration of penetrant in the surface layer of the film should be the same with liquid or saturated vapor, and in the steady state similar rates of permeation would be expected. It was decided, therefore, to check this phenomenon under carefully controlled steady state conditions. A series of measurements of the permeability constants was carried out at gradually increasing vapor pressures up to saturation followed by liquid penetrant itself. Since the logarithm of the permeability constant varies almost linearly with vapor pressure, it should be possible to demonstrate any marked changes in proceeding from the vapor to the liquid state.

Experimental

A modified version of the conventional high vacuum method was used for the measurements of the permeability constants. Details of the equipment have recently been published (2), and will not be repeated here. The method of operation ensures the accurate measurement of the correct pressures and temperatures and also the steady removal of vapor from the downstream side of the permeability cell. The actual determinations were repeated after considerable lapses of time to make sure that true steady state values were obtained.

Blown polyethylene film, density 0.923, thickness 0.035 mm., and a vulcanized unfilled natural rubber membrane, thickness 0.35 mm., were used. Freshly distilled benzene and cyclohexane were chosen as penetrants for the polyethylene study and acetone and acetonitrile for the determinations using the rubber membrane.

Results and Discussion

(a) Polyethylene. The results obtained with cyclohexane and benzene at 0° and 20°C. are presented in Figures 1 and 2 in the form of plots of the logarithm of the permeability constants versus the relative vapor pressure. The curves are linear up to relative vapor pressures of about 0.65 and are similar to those previously reported (5). The saturated vapor pressure values lie on a smooth curve with the other vapor values but the liquid values are somewhat higher. It was found that the liquid values gradually increased with time up to the constant values recorded on the graphs. On pumping out the film and remeasuring the permeability at progressively increasing vapor pressures a different curve was obtained and the saturated vapor and liquid values then became identical. Finally, samples of film were preconditioned by soaking in benzene for 24 hr. at room temperature. The films were then pumped out and the series of measurements repeated. The results are included in Figure 2. It can be seen that the saturated vapor and the liquid values are now identical and all points lie on a smooth curve.

The differences between liquid and saturated vapor permeabilities obtained using unconditioned film are probably due to the "conditioning" effect of the liquid penetrant. Such changes are undoubtedly due to re-

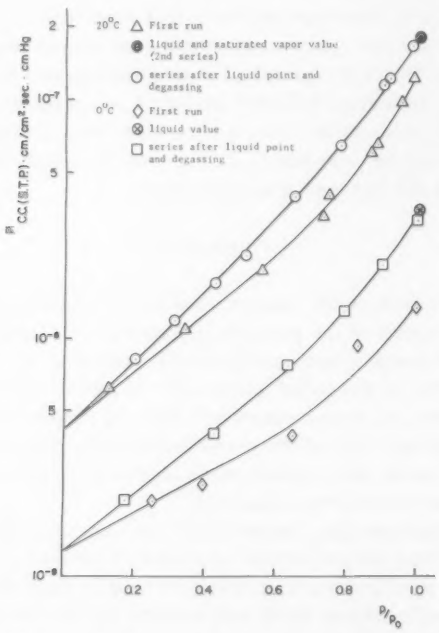

Fig. 1. The permeability of polyethylene to cyclohexane.

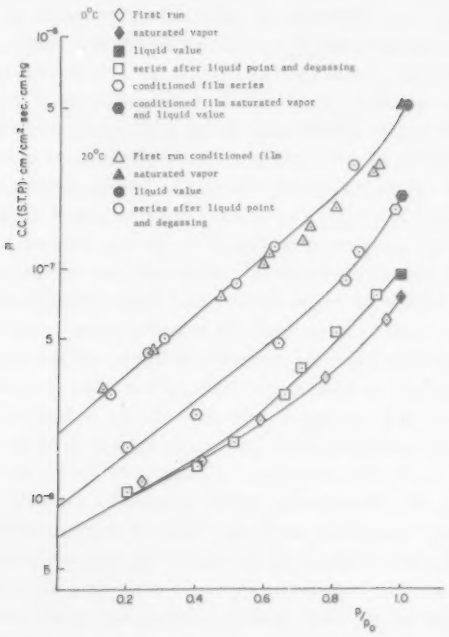

Fig. 2. The permeability of polyethylene to benzene.

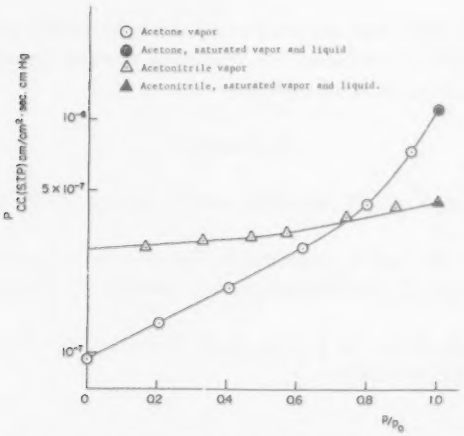

Fig. 3. The permeability of vulcanized rubber to acetone and acetonitrile at 25°C.

laxation phenomenon and minor morphological changes in the film. These effects have been investigated and discussed in detail by Michaels (5) in respect to much more drastic solvent treatments. Once the films have been conditioned the liquid points become identical with the saturated vapor points as would be anticipated on thermodynamic grounds.

In view of the minor differences found with unconditioned polyethylene films, a number of measurements were carried out using vulcanized rubber when no conditioning effects should be encountered.

(b) Vulcanized Rubber. The results obtained with acetone and acetonitrile vapor are presented in Figure 3. It can be seen that, although similar shaped plots were obtained, there were no differences between the liquid and saturated vapor values and that all the permeability constants lie on a smooth curve with the relative vapor pressure.

It is interesting to note the different behavior of the two penetrants. Acetone has a molar volume about 40% greater than acetonitrile and swells rubber to 19% compared with only 2% for acetonitrile (6). Consequently, at low relative vapor pressures rubber is less permeable to the more bulky molecule, acetone. As the sorption increases, at higher vapor pressure, the plasticizing effect increases the diffusivity (3) and the permeability to acetone surpasses that of acetonitrile.

It is probable that difficulties in measuring correctly the pressures and temperatures with saturated vapor, of removing all vapor from the downstream side of the cell, and of maintaining steady state conditions account for the anomalous results sometimes found with these systems.

We would like to thank Mr. J. L. Williams for his help with the experimental work.

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RADICAL HOMOPOLYMERIZATION OF 5-CYANOBICYCLO [2.2.1]-HEPT-2-ENE

1,2-Disubstituted ethylene monomers show little tendency to homopolymerize through radical mechanism as the result of the increased steric effect of the substituent (1). However, several investigators have reported that some cyclic ethylene derivatives, such as vinylene carbonate (2), acenaphthylene (3), maleic anhydride (4), maleic imide (5), bicyclo [2.2.1]-hepta-2,5-diene (6,7), and 2-carbethoxybicyclo [2.2.1]-hepta-2,5-diene (8) can induce radical homopolymerization.

We found that the endo and exo isomers of 5-cyanobicyclo [2.2.1]-hept-2-ene (CBH) could also homopolymerize in the presence of radical initiator. The present letter is concerned with the results of the homopolymerizations of the endo- and exo-CBH by dibenzoyl peroxide (BPO), di-tert-butyl peroxide (TBPO), and 2,2′-azobisisobutyronitrile (AIBN).

endo- and exo-CBH were synthesized by Diels-Alder's reaction of cyclopentadiene and acrylonitrile, followed by fractional distillation (9):

endo-CBH: b.p. 88.0-89.0°C./12mm. Hg, d_4^{20} 1.014, n_D^{30} 1.4872
exo-CBH: b.p. 80.0-80.5°C./12mm. Hg, d_4^{20} 1.005, n_D^{30} 1.4842

Bulk polymerizations were carried out in sealed glass tube by the addi-

TABLE I

Bulk Polymerizations of endo-CBH and exo-CBH

Expt. No.	Monomer[a]	Initiator, g.	Temp., °C.	Time, hr.	Conversion, %
1	endo-CBH	AIBN, 0.20	100	32	3.81
2	exo-CBH	AIBN, 0.20	100	32	3.79
3	endo-CBH	BPO, 0.20	100	36	6.19
4	exo-CBH	BPO, 0.20	100	36	5.12
5	endo-CBH	TBPO, 0.21	100	100	7.63
6	exo-CBH	TBPO, 0.21	100	100	5.66
7	endo-CBH	γ-Ray	0 ~ 10	288	0.5
8	exo-CBH	γ-Ray	0 ~ 10	288	0.3

[a]In all cases, 10 g. of the monomer was used.

TABLE II

Properties and Analytical Data of the Resulting Polymers

Expt. No.[a]	Polymer (initiator)[b]	m.p., °C.	Mol. wt., (n)[c]	Analyses,[d] % C	H	N
1	Poly-endo-CBH(AIBN)	100	410 (2.9)	78.58	7.29	12.89
2	Poly-exo-CBH(AIBN)	165	630 (4.7)	78.38	8.00	13.02
3	Poly-endo-CBH(BPO)	122	470 (3.0)	78.62	7.32	9.45
4	Poly-exo-CBH(BPO)	185	860 (6.2)	77.81	6.88	9.33
5	Poly-endo-CBH(TBPO)	210	750 (5.7)	78.89	7.51	11.19
6	Poly-exo-CBH(TBPO)	260[e]	970 (7.5)	78.61	7.70	11.03

[a]Expt'l. Nos. are the same in both Tables I and II.
[b]The initiators used in polymerization are indicated in parenthesis.
[c]Molecular weights of the polymers were determined by Rast method using camphor. (n) Indicates the average degree of polymerization calculated from $R(C_8H_9N)_n$, where R stands for initiator fragment.
[d]ANAL. Calcd. for $(C_8H_9N)_n$: C 80.67%, H 7.56%, N 11.76%.
[e]Melted with decomposition.

tion of radical initiators or γ-ray irradiation. The results are shown in Table I.

As can be seen from Table I, both endo- and exo-CBH monomers polymerized at a slow rate, while the endo-CBH polymerized faster than the exo-CBH in all cases. When we compared the activity of initiators for radical polymerization of CBH, the peroxide initiators (BPO and TBPO) were superior to the azo initiator (AIBN). Table II shows the results of melting point, molecular weight, and elementary analyses of the resulting polymers.

As can be seen from Table II, the molecular weights of the resulting polymers were quite low and these values were in agreement with those calculated from the nitrogen content in the polymer, by assuming that each polymer contained one initiator fragment. Their melting points increased with increasing their molecular weights from 100 to 260°C. In our previous studies on radical polymerizations of vinyl bicyclo [2.2.1]-heptane-2-carboxylate (10) and bornyl methacrylate (11), it was proved that the chain transfer to bicyclo [2.2.1]-heptane group in these monomers was very important. Accordingly, it is clear that the abstraction of tertiary hydrogen atoms in CBH by radicals is significant in these polymerizations.

The polymers in Expt. Nos. 1-5 in Table II were soluble in benzene-

methanol mixture, tetrahydrofuran, and dimethylformamide, while the polymer in Expt. No. 6 was soluble only in dimethylformamide. Infrared spectra of the resulting polymers showed the nitrile absorption band (2240 $cm.^{-1}$), but the absorption of the carbon-carbon double bond was not observed in the specific bands for nitrile, carbonyl, and ether groups due to initiator fragments. However, from the unsaturation determination of the polymers in Expt. Nos. 3-6 by the bromination method, these polymers were found to be about 20% unsaturated. These unsaturation contents and the molecular weights of the polymers indicate that each polymer contains one monomer unit possessing a double bond. This fact may be explained by the larger hydrogen abstraction ability of the CBH monomer by radicals as mentioned above.

Both CBH monomers could also copolymerize with styrene, vinyl chloride, vinyl acetate, acrylonitrile, and maleic anhydride. From the results of copolymerization with acrylonitrile, it was found that Q and e values for both CBH monomers were 0.07 and +0.28, respectively. More detailed results will be described in a future publication.

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EVALUATION OF VISCOSITY CONSTANTS

Several empirical expressions of the exponential binomial type have been proposed to describe the variation of the viscosity with polymer concentration, which fit with more or less success to experimental data. In general, one can write:

$$\eta_{sp}/c = [\eta] + a_1 c + a_2 c^2 + \ldots \quad (1)$$

If any of the foregoing expression holds, the coefficients a_i are related to each other and show some regularities such as:

$$a_1 = k_1[\eta]^2, \qquad a_2 = k_2[\eta]^3, \qquad \ldots \quad (2)$$

The slope constants k_j thus defined are frequently used in the qualitative discussion of the solution properties of polymers as a parameter, which is influenced by the shape and structure of polymer molecules and mutual interaction between solvent and polymer molecules.

In evaluating these constants obtained from the viscosity measurements of a dilute polymer solution, the following method is often used: we draw two curves of reduced viscosity versus concentration and inherent viscosity versus concentration. Intrinsic viscosity is determined from the intersection of the two curves on the axis of $c = 0$ by extrapolating the concentration to infinite dilution, and slope constants from the concentration dependence of the reduced viscosity. In this case, experimentally, the concentration terms of higher power than square are usually neglected, and intrinsic viscosity and slope constants are obtained graphically from the practically straight lines. Strictly speaking, however, the square concentration term cannot be neglected since it considerably affects the estimation of intrinsic viscosity and especially k_1.

The results obtained from polyacrylonitrile fraction in N,N-dimethylformamide are shown by the solid line in Figure 1 as an example of this method. Polyacrylonitrile used in this letter was prepared by a redox polymerization at 40°C., with ammonium persulfate as the initiator and sodium bisulfite as the activator, in all-glass apparatus. Fractionation was carried out at 35°C. by using dimethyl sulfoxide-toluene as the solvent-precipitant system (1).

Concentration dependence of inherent viscosity is empirically expressed as follows:

$$\ln\eta_r/c = [\eta] - b_1 c + b_2 c^2 + \ldots \quad (3)$$

Equation (3) is transformed to eq. (4) by the series expansion of

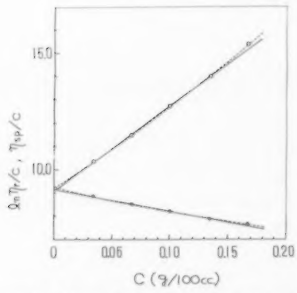

Fig. 1. Viscosity data for polyacrylonitrile fraction in N,N-dimethylformamide at 35°C.

natural logarithm.

$$\eta_{sp}/c = [\eta] + ([\eta]^2/2 - b_1)c + (b_2 - [\eta]b_1 + [\eta]^3/6)c^2 + \ldots \qquad (4)$$

Replacement of b_1 by $\beta[\eta]^2$ yields eq. (5) by comparison with eq. (1).

$$k_1 + \beta = 1/2 \qquad (5)$$

However, k_1 and β obtained from the solid lines in Figure 1 were 0.43 and 0.12, respectively, and the sum of them was not 1/2 despite the fact that the plots of the reduced viscosity versus concentration and inherent viscosity versus concentration give essentially straight lines.

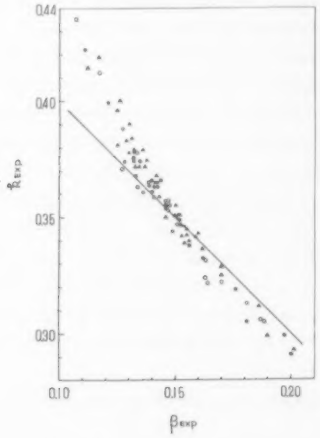

Fig. 2. Plot of k_{exp} against β_{exp} for polyacrylonitrile fractions in N,N-dimethylformamide: (O) at 20°C., (●) at 35°C., (Δ) at 50°C., and (▲) at 70°C..

This is because the contribution of the concentration terms of higher power are neglected for the analysis of viscosity data. In the following discussion, $[\eta]$, a_1, k_1, and β, which were obtained by neglecting the contribution of the concentration terms higher than square power, are denoted as $[\eta]_{exp}$, a_{exp}, k_{exp}, and β_{exp}.

In Figure 2, furthermore, the relationship between k_{exp} and β_{exp} for the polyacrylonitrile fractions in N,N-dimethylformamide is shown. The values of k_{exp} and β_{exp} deviate pretty much from the straight line of $k_{exp} + \beta_{exp} = 1/2$, and k_{exp} and $(k_{exp} + \beta_{exp})$ are seen to increase with increasing molecular weight (molecular weight dependence is not shown in the figure).

The slope, a_{exp}, is expressed as follows within the polymer concentration up to c_j:

$$a_{exp} = [(\eta_{sp}/c_j) - [\eta]_{exp}]/c_j \tag{6}$$

Hence, k_{exp} ($= a_{exp}/[\eta]^2_{exp}$) is expressed by the following equation:

$$k_{exp} = ([\eta] - [\eta]_{exp})/c_j[\eta]^2_{exp} + (a_1 + a_2c_j + \dots)/[\eta]^2_{exp} \tag{7}$$

Similarly, β_{exp} is as follows.

$$\begin{aligned}\beta_{exp} &= b_{exp}/[\eta]^2_{exp} \\ &= ([\eta]_{exp} - [\eta])/c_j[\eta]^2_{exp} + (b_1 - b_2c_j + \dots)/[\eta]^2_{exp}\end{aligned} \tag{8}$$

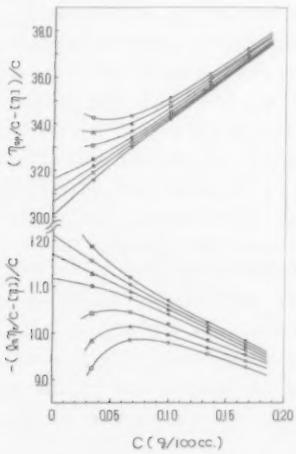

Fig. 3. $(\eta_{sp}/c - [\eta])/c$ and $(\ln \eta_r/c - [\eta])/c$ for several values of intrinsic viscosity plotted against c. The data previously shown in Fig. 1 were used here. Values of intrinsic viscosity in this case are as follows: (O) 9.17; (Δ) 9.19; (□) 9.21; (●) 9.23; (▲) 9.24; (×) 9.25; (■) 9.26.

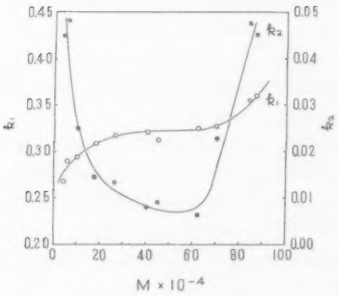

Fig. 4. k_1 and k_2 for a series of polyacrylonitrile fractions in N,N-dimethylformamide at 35°C. plotted against the molecular weight.

Using only the concentration terms not greater than c^2 in eq. (1), eq. (9) is derived from eqs. (7) and (8).

$$k_{exp} + \beta_{exp} = 1/2\ ([\eta]^2/[\eta]^2_{exp}) + (k_1 - 1/3) \times ([\eta]^3 c_j/[\eta]^2_{exp}) \quad (9)$$

Equation (9) shows that $(k_{exp} + \beta_{exp})$ could be 1/2 in the system where k_1 is smaller than 1/3, even provided some errors were made in the experiment. Therefore, we should be very careful in the evaluation of the experimental results. In the results of Figure 2, the $k_{exp} \sim \beta_{exp}$ plots make a curve which crosses the straight line of $k_{exp} + \beta_{exp} = 1/2$ at $k_{exp} \doteqdot 0.35$. This means that there is an overestimation of at least about 5% even in some data of Figure 2 where $(k_{exp} + \beta_{exp})$ is 1/2.

The intrinsic viscosity and k_1 can be estimated more properly by considering up to the concentration terms of c^2 in the eqs. (1) and (3): we first plot the values of $(\eta_{sp}/c - [\eta])/c$ and $(\ln \eta_r/c - [\eta])/c$ against c, respectively, then we change $[\eta]$ value little by little so that the plots make essentially a straight line and the sum of k_1 and β is 1/2. The intercepts give a_1 and b_1, which in turn, give k_1 and β in conjunction with intrinsic viscosity. The slopes of the curves are a_2 and b_2, respectively. Figure 3 shows this operation for the experimental result in Figure 1. From the results in Figure 3, 9.25, 30.8, and 36.0 were obtained for $[\eta]$, a_1 and a_2, respectively, which satisfy the above-mentioned conditions. The dashed curves in Figure 1 show the result when the above figures were substituted in eq. (1)(terms higher than c^3 were neglected). This explains the experimental results more reasonably than the solid line obtained by considering only the first-order concentration term.

Among many data shown in Figure 2, some obtained by 35°C.-measurements were recalculated according to the above method, and k_1's and k_2's thus obtained were plotted against molecular weight, as shown in Figure 4. The molecular weights were calculated according to the

following equation (2):

$$[\eta] = 2.78 \times 10^{-4} M^{0.76} \quad (10)$$

As is seen in Figure 4, k_1 and k_2 for polyacrylonitrile in N,N-dimethylformamide solution show a very complicated molecular weight dependency. It is known that the intrinsic viscosity of polyacrylonitrile in dimethylformamide decreases with the increasing temperature (3-6), and this fact was also supported with these experimental results, but it was found that the observed k_1 and k_2 are independent of the temperature used within experimental error. This problem will be discussed in detail in another paper.

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HIGH CONVERSION POLYMERIZATION OF METHYL METHACRYLATE

After beginning to polymerize in a normal fashion, the polymerization of methyl methacrylate accelerates remarkably after about 10–20% conversion, and at the same time the molecular weight of polymer being formed greatly increases. This phenomenon, termed the "gel effect," has been explained by Trommsdorff and others (1,2) on the basis of a reduction in the rate of termination resulting from the immobility of the growing polymer radicals accompanying increased viscosity. The reactive chain ends can no longer come together readily for bimolecular termination, but the small monomer molecules can still diffuse in order for chain growth to continue. However, a satisfactory kinetic scheme which includes the high conversion polymerization has not been put forward. The purpose of this note is to present a simple quantitative interpretation which will account for the high conversion polymerization of methyl methacrylate.

Initial polymerization rates for methyl methacrylate is

$$-dM/dt = k_p[P\cdot][M] \tag{1}$$

where $[P\cdot]$ represents the total concentration of all chain radicals, and [M] represents the monomer concentration. Many investigators have shown that the rate constant for termination is greatly diminished at high conversions (3-5), whereas the rate constant for propagation remains constant within experimental error (6). On the other hand, Burnett (7) considered the "gel effect" as a radical concentration phenomenon.

If radicals can be trapped in a highly viscous system, and become unable to contact one another in order to undergo mutual destruction, this would mean that the concentration of radicals would increase continually, as the monomers are consumed. At the limiting conversion radicals are so enmeshed in the polymer that they are rendered inaccessible to the monomer.

As a first approximation we could suppose the concentration of radicals to be proportional to the monomer concentration consumed after the "gel effect." The ideas stated above can be expressed mathematically in the following manner:

$$[P\cdot] = K(x - b) \qquad (x > b) \tag{2}$$

where K is a constant, x is the conversion of the monomer and b is the conversion at which the "gel effect" begins. It has already been stated

that the small monomer molecules can still diffuse in order for chain growth to continue until the limiting conversion.

$$[M] = (a - x) \qquad (x < a) \tag{3}$$

where a is the limiting conversion.

As the rate constant for propagation k_p is still unchanged over the advanced stage of polymerization (6), we can use eq. (1). From eqs. (1), (2), and (3) we have

$$dx/dt = k_pK(x - b)(a - x) \tag{4}$$

Integration of equation (4) leads to

$$[1/(a - b)] \ln [(x - b)/(a - x)] = k_pKt + C \tag{5}$$

where C is a constant.
Equation (5) requires that the plot of

$$[2.3/(a - b)] \log [(x - b)/(a - x)]$$

against t over the accelerated phase of the reaction should be linear. The solution of eq. (5) for x as a function of t yields:

$$x = [a \exp(a - b)(k_pKt + C) + b]/[1 + \exp(a - b)(k_pKt + C)] \tag{6}$$

This gives the S-shaped curve typical of the gel effect (see Fig. 1).

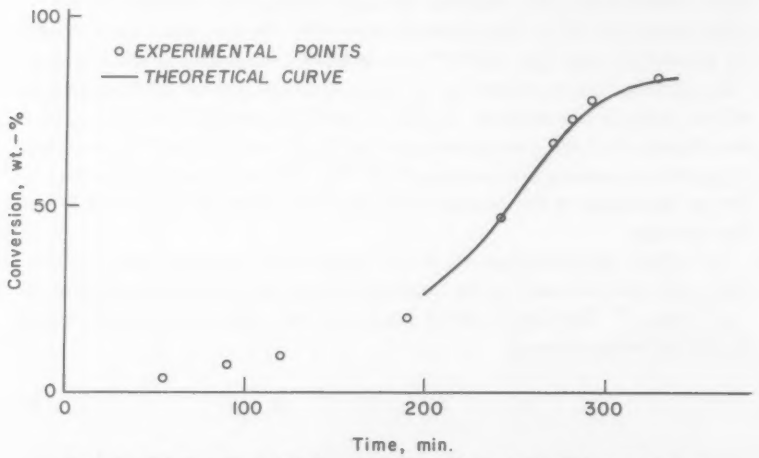

Fig. 1. The course of polymerization of methyl methacrylate at 60°C. in the presence of 0.2% benzoyl peroxide.

TABLE I

Polymerization of Methyl Methacrylate at 60°C. in the Presence of 0.2% Benzoyl Peroxide (1).

No.	Reaction time, min.	Conversion, %
1	55	3.5
2	90	7.1
3	120	9.8
4	190	20.0
5	240	46.2
6	270	65.8
7	280	73.0
8	290	77.5
9	325	82.5

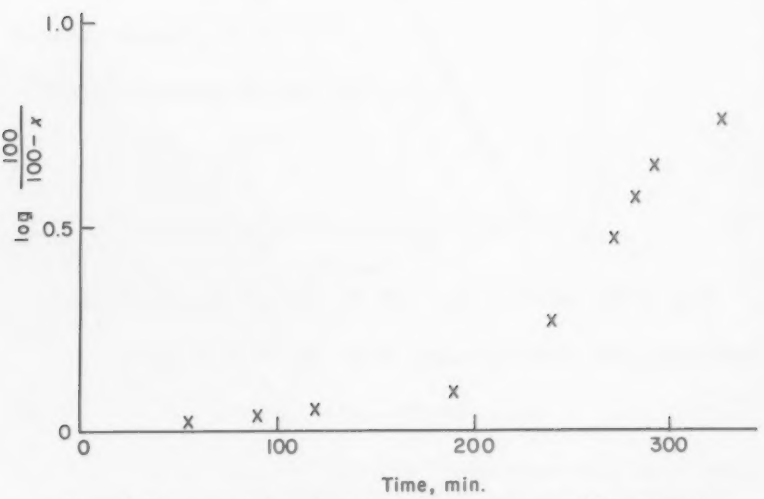

Fig. 2. Polymerization of methyl methacrylate at 60°C. plotted as a first-order reaction.

Trommsdorff (1) followed the course of polymerization of methyl methacrylate with time. His results are shown in Table I. The temperature rise was negligible in the experiments of Trommsdorff and so isothermal conditions were maintained. The value of "a" is obtained from the conversion-time curve (Fig. 1). It is found to be 85%. The value of "b" is obtained from the plot of $\log[100/(100-x)]$ against t (Fig. 2). The conversion at which the pronounced deviation from the first-order course sets in corresponds to a polymer concentration of 20%. Hence "b" is

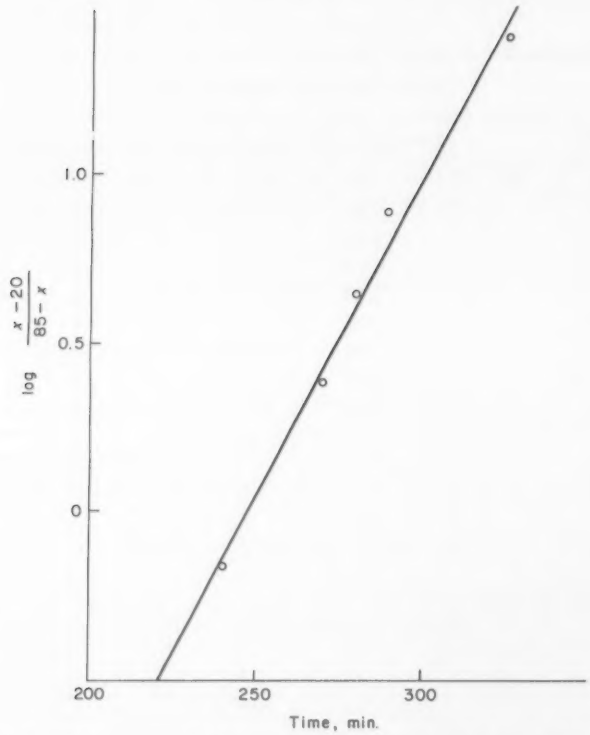

Fig. 3. The quantity $\log[(x-20)/(85-x)]$ as a function of time.

found to be 20%. From the values of "a" and "b," we obtain

$$\log[(x-20)/(85-x)] = At + B \qquad (7)$$

where A and B are constants.

Figure 3 shows the plot of $\log[(x-20)/(85-x)]$ versus t. Over the accelerated range studied the plots are satisfactorily linear. This linear relationship suggests the validity of eq. (5). We have plotted our calculated points in Figure 1, and the solid curve is obtained from these calculated points. It is clear that there is good agreement between the experimental results and the independently developed theory.

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A GLASS TEMPERATURE RELATIONSHIP

In a recent paper (1) it was postulated that

$$(\alpha_L - \alpha_G)\, T_g = K_1 \tag{1}$$

where α_L and α_G are the respective cubic thermal expansion coefficients above and below the glass temperature, T_g is the dilatometric glass temperature in °K., and K_1 is a constant. This had been put forth in an attemp to improve an earlier relation (2)

$$\alpha_L T_g = K_2 \tag{2}$$

where K_2 is another constant.

Another relation is now proposed

$$1/2[(dv/dT)_L + (dv/dT)_G]\, T_g/v_g = K_3 \tag{3}$$

where $(dv/dT)_L$ and $(dv/dT)_G$ are the volume-temperature coefficients, v_g is the specific volume at the glass temperature, and K_3 is a constant parameter. It is considered likely at this time that K_3 will be a function of the types of bonds occurring in the polymer chain, and that it will approach a constant value for each class of polymers with the same backbone structure. The form of eq. (3) is based upon the definition of the limiting value of a step function at the discontinuity.

The physical interpretation of eq. (3) is compatible with the fractional iso-free volume state concept which is one of the currently accepted explanations of the glass "transition".

It is noted that eq. (3) gives satisfactory agreement for the poly-n-alkyl methacrylates without the use of any additional stipulations as was required by eq. (1).

It is acknowledged that part of this work was conceived at Brown University while the author was on a postdoctorate fellowship with Prof. J. H. Gibbs.

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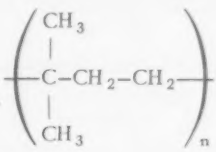
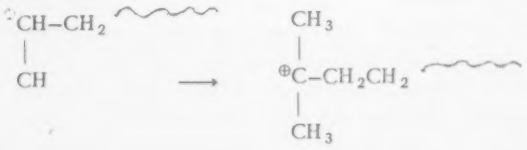
THE CATIONIC POLYMERIZATION OF 3-METHYLBUTENE-1 AND 1,1-DIMETHYLCYCLOPROPANE

The cationic polymerization of 3-methylbutene-1 at low temperatures has been shown by Kennedy to yield a product having a fundamentally different structure from that of the vinyl addition polymer obtained with Ziegler-Natta catalysts (1). NMR data indicate that the polymer consists predominently of repeating units:



Such a structure would result from an intramolecular hydride transfer in the propagation step,



which gave exclusively the more stable tertiary carbonium ion. This is in contrast to the cationic polymerization of propylene and butene-1 where several different hydride transfers occur leading to complex products (2).

Pines has reported that 1,1-dimethylcyclopropane does not undergo ring-expansion in the presence of aluminum bromide (2). Instead, polymerization occurs. In this reaction, cleavage of the cyclopropyl ring by an attacking carbonium ion must take place at the 1,2-carbon-carbon bond:

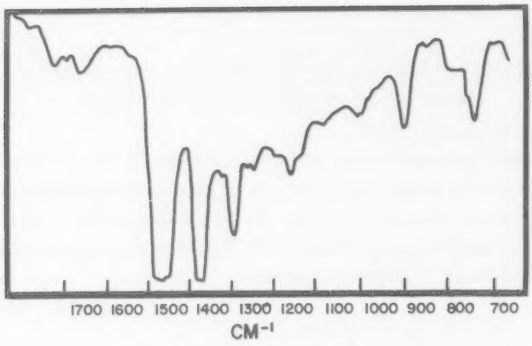


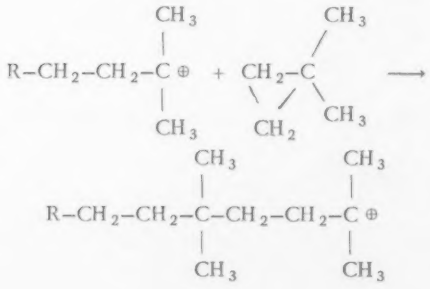
Fig. 1. Polymer from 1,1-dimethylcyclopropane.

TABLE I

Major Absorptions in the Infrared Spectra of Polymers from 3-Methylbutene-1 and 1,1-Dimethylcyclopropane

3-Methylbutene-1 frequency,[a] cm.$^{-1}$		1,1-Dimethylcyclopropane frequency, cm.$^{-1}$	
750	S	752	S
907	S	905	S
927	M	925	M
1088	W	1172	M
1170	M	1298	S
1298	S	1650	W
–		1720	W

[a] S = strong; M = medium; W = weak.



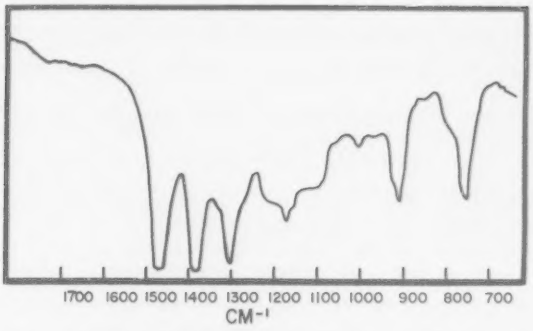


Fig. 2. Polymer from rearrangement polymerization of 3-methylbutene-1.

The polymerization of 1,1-dimethylcyclopropane should lead, therefore, to a polymer the structure of which is identical to that proposed for the product of the cationic polymerization of 3-methylbutene-1. The identity of the two polymers would consequently provide additional evidence for the hydride shift in the latter reaction.

0.6 Mole of 3-methylbutene-1 was polymerized in 250 ml. of ethyl chloride at −100°C. by 0.004 mole of aluminum chloride. The polymer had a molecular weight by osmometry of 13,300 and the infrared spectrum shown in Figure 1. Major absorptions in this spectrum are given in Table I. Polymers having the same infrared spectrum but molecular weights of 3-4000 were prepared using ethylaluminum dichloride at −78°C.

1,1-Dimethylcyclopropane, prepared by the Gustavson method (4), was polymerized in bulk at −50°C. by aluminum bromide (0.026 mole $AlBr_3$/ mole monomer). The infrared spectrum of the product (M.W. 1000) is shown in Figure 2 and the major absorptions are listed in Table I. Polymerizations in ethyl chloride solvent gave similar products as did those using aluminum chloride catalyst. Temperature had little effect, polymers prepared at −50° and 0°C. having the same infrared spectra and approximately the same molecular weights. Below −50°C., no reaction took place. Boron trifluoride-ether complex did not polymerize 1,1-dimethylcyclopropane under any conditions. The ring also could not be opened by ionizing radiation, the monomer being recovered unchanged after a 50 Mrad. dose in both the liquid (−9°C.) and solid (−121°C.) states.

Comparison of the infrared spectra of the polymers from these two reactions shows they have essentially the same structure. The absorptions between 1650 $cm.^{-1}$ and 1750 $cm.^{-1}$ in the polymer from 1,1-di-

methylcyclopropane probably arise from terminal unsaturation while the the shoulder at 850 cm.$^{-1}$ may be due to the cyclobutane ring (5). This suggests that termination may occur, in part, by ring expansion. All the major absorptions in this polymer must arise from the $-\mathrm{C}(\mathrm{CH_3})_2-\mathrm{CH_2}-\mathrm{CH_2}-$ unit. Consequently, this must be the predominating structural unit in the polymer obtained from 3-methylbutene-1.

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POLYMER LETTERS VOL. 1, PP. 317-321 (1963)

MEASUREMENT OF GLASS TRANSITION TEMPERATURES OF POLYMERS BY A DIFFERENTIAL PRESSURE TRANSDUCER

Every amorphous polymer has a narrow temperature range above which it exists as a viscous or rubbery material and below which it is hard and relatively brittle. At this temperature, called the glass transition temperature, T_g, several physical properties such as heat capacity, dielectric constant and thermal expansion coefficient show an abrupt change. The glass transition temperature of polymers is most frequently measured by determining the change in the thermal expansion coefficient using a dilatometric technique (1). This technique, although precise, is tedious and time-consuming, particularly when the approximate value of the glass transition is unknown. Another difficulty of a dilatometric method is the need of a confining liquid. Mercury which is most commonly used can lead to difficulties if there is improper wetting of the polymer thus creating voids. Also, because of the comparatively high freezing point of mercury, −38.9°C., other confining liquids such as isooctane must be used at low temperatures with the subsequent danger of polymer swelling. For these reasons it was desired to develop an apparatus capable of measuring glass transition temperatures automatically and which would use air, or an inert gas as the confining medium.

The continuous recording glass transition apparatus described herein utilizes a differential pressure transducer to detect changes in pressure between two containers, one holding the polymer sample and one with air, for reference. In this closed system the change in pressure is directly related to the change in volume of the polymer sample. The voltage from the transducer is plotted on one axis of an X-Y recorder and the emf from a thermocouple is plotted on the other axis. The glass transition temperature is the point at which the traced pressure-temperature line shows an abrupt change in slope.

In Figure 1 is shown a photograph of the complete apparatus. A Dynisco PT 14-05 differential pressure transducer with a maximum range of 0.5 psi is connected to the sample and reference cells by a coiled length of stainless steel tubing, 1/16 in. ID. The purpose of the thin tubing was to eliminate pressure fluctuations due to temperature gradients in the connecting tubing. The sample and reference cells were 1/4 in. ID copper test tubes, approximately 4.5 in. long, made by pinching and soldering one end. The other end of the tube was attached to the stainless steel tubing by a flared tube fitting. The sample cell was discarded after each use.

In order to provide a thermocouple environment comparable to that of

Fig. 1. Continuous recording glass transition apparatus.

the polymer in the sample tube, the thermocouple wires were inserted into a similar 1/4 in. ID copper test tube placed between the sample and reference cells. The thermocouple wires were surrounded by a tightly packed polyurethane foam with a very low glass transition temperature.

The transducer excitation voltage was provided by a 6 v. battery and the output of the transducer connected directly to the Y-axis of a Leeds & Northrup 69950 Speedomax G, X-Y recorder having a Y-axis range of −5 to +5 mv. full scale. The recorder X-axis was connected to a copper-constantan thermocouple through an ice junction. Its sensitivity range could be continuously adjusted from 0.5 mv. full scale to 10 mv. full scale. In addition, the thermocouple emf could be nulled with a bucking voltage, so that any temperature could be used as the zero point of the recorder. The exact bucking voltage was measured with a Leeds & Northrup 8686 millivolt potentiometer.

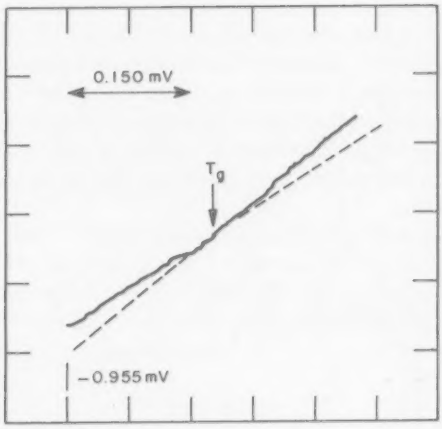


Fig. 2. Pressure-temperature trace for polyvinylidene chloride, $T_g = -20.6°C.$

The reference and sample cells were deeply immersed in a well-stirred and insulated oil bath whose temperature rise could be programmed for any predetermined rate of change. For glass transitions below room temperature a 4 liter Dewar flask containing a mixture of acetone-Dry Ice was used. The bath was equipped with a stirrer and a low-wattage immersion heater controlled by a Powerstat. This arrangement was found satisfactory without the need for actual temperature programming. Heating rates of approximately 0.1°C./min. were used throughout most of this work. The average polymer sample size was 1 g.

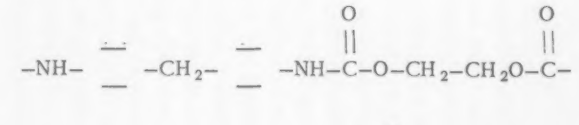
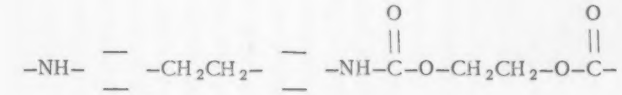
The most reliable results were obtained when the sample cell contained as little free air-space as possible. This was most readily accomplished by using powdered polymers, or solid plugs fitting snugly into the sample tube. When granulated polymers or polymer chips were used, detection of glass transition temperatures was not possible because of insufficient change in slope. As for standard dilatometric methods, it is important to remove all traces of solvent adsorbed on the polymer; this is especially critical in the present method because of the extreme sensitivity to very small pressure changes.

A typical pressure-temperature trace obtained from the recorder is shown in Figure 2. The glass transition temperature was determined by the intersection of the two straight lines drawn over the actual traces. The T_g value of −20.6°C. thus obtained for polyvinylidene chloride is in good agreement with the value of −18.0°C. obtained by Boyer and Spencer (2) using a dilatometric technique.

The reliability of the values obtained for a number of different poly-

TABLE I

Comparison of Glass Transition Temperatures Obtained with a Differential Pressure Transducer and Those Obtained by Volume Dilatometry

Polymer	Glass transition, °C.		Reference
	Diff. press. transd.	Volume dil.	
Polyvinylidene chloride	−20.6	−18.0	(2)
Linear polyethylene (Marlex 50)	−24.4	−21.0	(3)
Polyvinyl acetate	29.0	29.0	(4)
Copolyether-urethane	−68.1	−68.2	(5)
	94.2	92.7[a]	(6)
	116.1	116.9	(6)

[a]Vibrating reed method gave a value of 90.

mers using the recording T_g apparatus is further demonstrated in Table I. The ease and accuracy of this method, freedom from errors that can arise from confining liquid-polymer interactions, and a virtually unlimited temperature range make possible a systematic investigation of the glass transition temperature of a large number of polymer and copolymer systems under a rigorously standardized set of conditions. We are currently undertaking such a program in order to correlate the effect of molecular structure on the glass transition temperature of polymers.

The authors wish to acknowledge valuable discussions with Norman Fishman and Leon E. Hiam of these laboratories who are primarily responsible for the initial conception of this application of a differential pressure transducer. The help of N. F. Humeny of the Leeds & Northrup Co. is also gratefully acknowledged.

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REMARKS ABOUT SEQUENCE DISTRIBUTION FUNCTIONS. THEIR RELATION TO COPOLYMER CRYSTALLINITIES.

Sequence lengths distributions in copolymer chains are of interest because of their influence on physical and technological copolymer properties. Our knowledge of them is founded mainly on theoretical derivations based upon kinetic and statistical considerations since experimental determinations are difficult, and have so far been carried out only in a few cases.

Theoretical studies of the subject have been contributed by several investigators (1-5). A few more additional relations may be pointed out here.*

Alfrey and Goldfinger (1) have deduced equations for the probability of two succeeding monomer units of type 1 in a copolymer chain:†

$$P_{11} = r_1[M_1]/(r_1[M_1] + [M_2])$$
$$P_{12} = [M_2]/(r_1[M_1] + [M_2]) = 1 - P_{11} \qquad (1)$$

The probability of a sequence of n units of monomer 1 is (1):

$$P_1(n) = P_{11}^{(n-1)} \cdot P_{12} \qquad (2)$$

The number average sequence length of 1-units (1):

$$\bar{n}_1 = \frac{\sum_1^\infty n \cdot P_1(n)}{\sum_1^\infty P_1(n)} = 1/(1 - P_{11}) = 1/P_{12} \qquad (3)$$

The weight average sequence length can be defined in analogy to weight average molecular weights as:

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*The following derivations are based upon the assumption that only the last monomer unit of a growing chain influences the addition of the next monomer unit. The work of Ham and others, which takes into account the influence of non-terminal units on the reactivity of active copolymer chains is not considered here.

†For simplicity all expressions are given for monomer units of type 1 only, but may analogously be formulated for type 2 units.

$$\bar{n}_{w_1} = \frac{\sum_1^\infty n^2 \cdot P_1(n)}{\sum_1^\infty n \cdot P_1(n)} = (1 + P_{11})/(1 - P_{11}) \tag{4}$$

Defining a sequence heterogeneity analogously to molecular weight heterogeneity according to Schulz (6):

$$h_{1_{sequ.}} = (\bar{n}_{w_1}/\bar{n}_1) - 1 \tag{5}$$

it follows from eqs. (3), (4), and (5):

$$h_{1_{sequ.}} = P_{11} \tag{6}$$

$$0 < P_{11} < 1 \text{ if } r_1 > 0$$

The extremes $P_{11} = 0$ and $P_{11} = 1$ correspond to homopolymer 2 and 1 respectively. If $r_1 = 0$ and consequently $P_{11} = 0$, no monomer–1 sequences higher than 1 occur.

The probability function of the mass distribution of 1-units is (5):

$$m_1(n) = n \cdot P_1(n) \tag{7}$$

with a maximum at*

$$n_{1_{max}} = -1/\log_e P_{11} \tag{8}$$

Copolymerizing binary systems, the sequence lengths distributions of the two components become identical at

$$[M_1]/[M_2] = \sqrt{r_2/r_1} \tag{9}$$

In any multicomponent system of monomer units which are capable of crystallizing as homopolymer or in sufficiently long sequences, the crystallinity† of the copolymer should be related to the quotient Q of the sum of monomer units in sequences equal to, and larger than a, divided by the sum of all monomer units of the considered type present, a being the minimum sequence length required for crystallization.

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*The mass distribution function eq. (7) is treated as a steady function.

†The effect of steric irregularities in copolymer sequences on the crystallinity is not considered here. This is to be discussed in terms of a steric copolymerization.

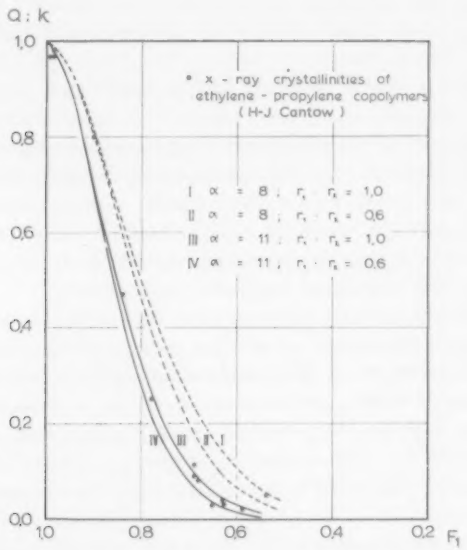

Fig. 1. Degree of crystallinity from sequence distributions. (The values of the experimental degree of crystallinity κ of the copolymers refer to $\kappa_{polyethylene} = 1.0$.)

$$Q_1 = \frac{\sum_{1}^{\alpha} n \cdot P_{11}^{n-1} \cdot P_{12}}{\sum_{1}^{\infty} n \cdot P_{11}^{n-1} \cdot P_{12}} = 1 - \frac{\sum_{1}^{\alpha-1} n \cdot P_{11}^{n-1} \cdot P_{12}}{\sum_{1}^{\infty} n \cdot P_{11}^{n-1} \cdot P_{12}} = \alpha \cdot P_{11}^{\alpha-1} - (\alpha - 1) \cdot P_{11}^{\alpha} \quad (10)$$

It should be noted that, at given copolymer compositions, P_{11} and consequently Q_1 do not depend on the individual values of the reactivity ratios r_1 and r_2, but on the product $r_1 \cdot r_2$. This can easily be seen by combining eq. (1) with the known copolymer composition equation:

$$d[M_1]/d[M_2] = ([M_1]/[M_2]) \cdot (r_1[M_1] + [M_2])/([M_1] + r_2[M_2]) \quad (11)$$

which leads to

$$d[M_1]/d[M_2] = 1/[P_{11}(r_1 r_2 - 1) + r_1 r_2(P_{11}^{-1} - 2) + 1] \quad (12)$$

Figure 1 shows Q_1 plotted as a function of the mole fraction (F_1) of component 1 in the copolymer. The curves correspond to (I) $\alpha = 8$;

$r_1 \cdot r_2 = 1.0$; (II) $\alpha = 8$; $r_1 \cdot r_2 = 0.6$; (III) $\alpha = 11$; $r_1 \cdot r_2 = 1.0$; and (IV) $\alpha = 11$; $r_1 \cdot r_2 = 0.6$. The position of the curves is not highly sensitive to a change of $r_1 \cdot r_2$ from 0.6 to 1.0.

Applying eq. (10) to ethylene-propylene copolymers prepared with organometallic complex catalysts systems,* an appreciation of the ability of the catalyst to build up statistical copolymer chains can be derived from x-ray measurements of copolymers richer in ethylene than in propylene, since polyethylene crystallizes readily with no tacticity being involved. In the case of statistical copolymers, a minimum sequence length required for crystallization can be estimated from a comparison of experimental and calculated degrees of crystallinity.

Cantow (9) has recently reported x-ray crystallinities of several ethylene-propylene copolymers† in relation to the ethylene-content. The evaluation in terms of eq. (10) yields an approximate value of $\alpha = 11$, as Figure 1 shows. Taking into account that x-ray measurements should yield smaller degrees of crystallinity than expected from the assumptions underlying eq. (10), a minimum ethylene sequence able to crystallize in the order of 9 or 10 is considered a reasonable estimation, so far as x-ray crystallinity is concerned.§ Crystallinities calculated from refractive index measurements (11) which are generally smaller than those determined by x-rays can be treated in the same way.

The results shown in Figure 1 indicate statistical chain structures of the copolymers investigated, demonstrating the potential capability of Ziegler-Natta catalyst systems to produce statistical sequence distributions which correspond to those obtained by free radical copolymerization.

Further systematic studies are presently being carried out.

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*Reactivity ratios for the ethylene-propylene copolymerization with various Ziegler-Natta catalysts have been reported by Natta et al. (7) and Bier et al. (8). The corresponding values of $r_1 \cdot r_2$ range from approximately 0.6 to 1.2.

†$r_1 \cdot r_2$ according to Bier (loc. cit.) ranging from 0.6 to 1.0.

§This value differs somewhat from Natta's statement (10) that C_2H_4-sequences of at least 15 monomer units are necessary for crystallization.

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ANIONIC GRAFTING REACTIONS

Preparation of graft copolymers has recently become of great interest, but most of the methods described in the literature do not allow a detailed characterization of both the polymer-backbone and the graftings: We have developed (1) a method of grafting which is comparatively adequate for the synthesis of graft copolymers of known degree of grafting, and in which independent determinations of the molecular weights of the backbone and of the graftings are rendered possible. Such well-characterized copolymers are extremely useful as model substances for solution studies, some of which have already been published (2). In the present note, our aim is to give some information on polydispersity and fluctuations in composition within the samples obtained.

I. Principle of the Method

It is now well known that a characteristic feature of anionic polymerization in homogeneous phase is the lack of termination reaction. Polymers obtained by this method have carbanionic end-groups, and those react readily with a number of functions, like ester groupings or alkyl halides. Thus we have prepared monofunctional "living" polystyrene, ususing tetrahydrofurane as solvent and phenylisopropyl-potassium as initiator. We have then added the solution of this ω-carbanionic polymer to a solution of a polymer which can act as a polyfunctional deactivator: polymethylmethacrylate (PMMA) or polyvinylchloride (PVC). The reagents are mixed at $-78°C.$, and temperature is allowed to rise while efficient stirring is maintained during the grafting process. Polymerization and grafting reactions are carried out in dry inert atmosphere (argon). For the sake of comparison with results published recently by Mitzengendler, Andreeva, Sokolova, and Korotkov (3) we have run also a few experiments in toluene solution with butyllithium as initiator.

II. Experimental Results and Discussion

It can be seen from Table I that the grafting reaction takes place as expected, and that a wide range of graft copolymers have been thus obtained. The degree of grafting, i.e., the percentage of ester functions which have reacted, remains low ($< 10\%$). Nevertheless, copolymers of high styrene content and of high molecular weight could be prepared.

Fractionations have been carried out on several of our samples in order to evaluate the fluctuations in composition within a sample. The solvent-precipitant system was chosen in such a way that the copolymer

TABLE I

Grafting of Polystyrene onto Polymethylmethacrylate

No.	$\bar{M}_w$, PS grafting	$\bar{M}_w$, PMMA backbone	$\bar{M}_w$, Graft copolymer	No. of graftings per PMMA molecule
Y A	30,500	98,000	525,000	14
Y B	10,500	98,000	382,000	28
Y D	6,000	10,300	58,000	8
Y F	15,700	400,000	2,700,000	150
Y G	30,000	600,000	1,100,000	17
Y H[a]	8,000	100,000	650,000	69
Y BC	13,500	69,500	150,000	6
Y BD	7,600	69,500	221,000	20

[a]This experiment was run in toluene solution with BuLi as initiator.

TABLE II

Fractionation of PMMA–PS Graft Copolymers

Fraction No.	γ	Weight	% MMA in fraction	$\bar{M}_w$, of fraction	Degree of grafting, %
Y H					
1	0.649	0.190	25	1,150,000	3.7
2	0.659	1.200	18	830,000	5.5
3	0.673	0.920	16.5	680,000	6.3
4	0.688	0.725	13.4	425,000	8.1
5	0.704	0.395	12.6	230,000	8.7
6	0.726	0.310	11.45	140,000	9.7
7	0.760	0.220	11.45	90,000	9.7
8	0.858	0.110	0.0	11,000	
9	Methanol	0.480	0.0		
Y BD					
1	0.577	0.810	49	335,000	1.37
2	0.597	0.880	40.9	326,000	1.90
3	0.617	1.240	40.5	320,000	1.93
4	0.645	1.340	32.7	150,000	2.71
5	0.691	0.490	23	53,500	4.40
6	0.791	0.450	14.65	30,800	7.66
7	0.858	0.320	0.0	7,600	
8	Methanol	1.470	0.0		

TABLE III[a]

Fractionation of PS–PVC Graft Copolymer Y_2

Fraction No.	Weight	% Cl	% PVC	M_w fraction	Degree of grafting, %
1	0.460	23.25	40.93	320,000	1.2
2	0.640	16.82	29.61	274,000	1.88
3	0.390	13.75	24.21	239,000	2.61
4	0.515	12.37	21.78	134,600	2.99
5	0.145	9.87	17.38	41,000	3.9
6	0.410	2.55	4.49	16,500	
7	0.830	0.80	1.41	11,500	
8	0.530	0	0		
9	0.440	0	0		
10	0.580	0			

[a] M_w grafting = 7,500; M_w PVC = 72,000; M_w copolymer without PS = 230,500.

would precipitate first and the ungrafted homopolystyrene last. We used benzene-chlorobenzene (1:1) as solvent mixture and petrol ether as precipitant for the system PMMA–PS; benzene and methanol respectively for the system PVC–PS (see Tables II and III).

The results of our fractionations led us to the following results: (1) no homopolymethyl methacrylate (or PVC) has been formed in the sample; (2) 20–40% of the total polystyrene remains ungrafted. We do not know yet whether this is entirely due to impurities or whether there is some side-reaction; (3) if the homopolystyrene is discarded, the fluctuations in composition within a sample are not very high; (4) the higher the molecular weight of the backbone, the lower are the degrees of grafting. The fluctuations are small if the polydispersity of the backbone polymer is low.

The results obtained by the quoted Russian authors (3) are quite different from ours: they have found very wide distributions of composition within the copolymer samples. They also claim to have obtained degrees of grafting much higher than ours. As a result they assume that grafting is not a statistical phenomena. These discrepancies between the results obtained in Leningrad and in Strasbourg may be due to the fractionation method. Korotkov and his co-workers are using selective extraction for this purpose. This method seems quite unfit for copolymer fractionation because of the high solubility of copolymers in selective solvents of the corresponding homopolymers.

In order to get a more precise view of the fluctuations in composition within our samples, we have tried to evaluate independently the polydis-

TABLE IV

Molecular Weight Distributions in Copolymer Y_H

Fraction No.	% Copolymer	% Total MMA in sample	% Total PS in sample	M.W. $\times 10^{-3}$ copolymer	M.W. $\times 10^{-3}$ PMMA	M.W. $\times 10^{-3}$ PS
7	5.55	4.0	5.85	90	10.3	80
6	7.83	5.64	8.24	140	16	124
5	9.97	7.93	10.36	230	29	201
4	18.31	15.46	18.84	425	57	368
3	23.23	24.12	23.06	677	111.7	566
2	30.30	35.28	29.36	830	153.5	676
1	4.79	7.55	4.28	1150	288	863

TABLE V

Molecular Weight Distributions in Copolymer Y_2

Fraction No.	% Copolymer	% Total PVC in sample	% Total PS in sample	M.W. $\times 10^{-3}$ copolymer	M.W. $\times 10^{-3}$ PVC	M.W. $\times 10^{-3}$ PS
5	6.74	4.14	7.73	41	7.2	33.8
4	23.95	18.39	26.18	134	29.2	104.8
3	18.14	15.50	19.17	239	57.8	181.1
2	29.77	31.11	29.24	274	81.1	192.9
1	21.39	30.86	17.67	320	131	190.0

TABLE VI

Polydispersity in Graft Copolymers

	Backbone			PS			Copolymer
	$M_w \times 10^{-3}$	$M_n \times 10^{-3}$	M_w/M_n	$M_w \times 10^{-3}$	$M_n \times 10^{-3}$	M_w/M_n	M_w/M_n
Y H	108	64	1.69	469	320	1.46	1.44
Y BD	86	54	1.62	129	81	1.59	1.76
Y_2	81	44	1.85	154	108	1.46	1.49

persity of the backbone-polymer, and of the polystyrene part of the polymer. Only one assumption is necessary. The distribution of molecular weights in the "living" polymer must be narrow, i.e., the graftings are all equal in size. For each fraction, light scattering experiments have been carried out. In the case of PMMA–PS copolymers, the molecular weight of the PS-part of the polymer can be determined directly by operating in benzene solution, where the dn/dc of PMMA is approximatively zero. For the system PVC–PS the measurements have been carried out in tetrahydrofurane solution, since the dn/dc value is high, leading to the true molecular weight of the copolymer. From the molecular weight values of copolymer fraction and grafting, and from the analysis data for the fraction, the grafting degrees have been calculated. This leads us to the distribution of molecular weights of the PMMA and of the total PS within the sample. Results are shown in Tables IV and V.

From these data one can calculate the average values of the molecular weights, and the polydispersity index of each constituent of the graft copolymer (Table VI).

These results are in very satisfactory agreement with the values one of us (4) has obtained on several of these copolymers from light scattering data on unfractionated samples, according to a method developed by Benoît and Leng (5). Here the fluctuations in composition within a sample are detected by a series of measurements in solvents of different indices of refraction, and values of the polydispersity can be calculated from the results.

All of these experiments and calculations confirm that the anionic grafting process is a very suitable method which leads to well characterizable graft copolymers of satisfactory homogeneity in composition. From our results it appears that the grafting on a PMMA or PVC chain has a definite statistical character.

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ANALYSE VON COPOLYMEREN DURCH TRÜBUNGSPUNKT-MESSUNG

Zwischen dem Logarithmus der Fällungsmittel-Konzentration im 1. Trübungspunkt und dem Logarithmus der Polymer-Konzentration im 1. Trübungspunkt besteht eine lineare Beziehung (1). Bei Extrapolation auf einen Gehalt von 100% Polymer erhält man einen vom Molekulargewicht und folglich von der Molekulargewichtsverteilung unabhängigen Parameter $(c_F)_\infty$ (1,2), der einem kritischen Punkt für binäre Gemische entspricht. Drückt man die Zusammensetzung der Lösungsmittel /Fällungsmittel-Mischung in diesem Punkt als Volumbruch aus, so entspricht dieser Volumbruch ψ_{crit} einem θ-Lösungsmittel (2). Bei orientierenden Versuchen an Polymethylmethacrylaten verschiedener Taktizität wurden ferner Zusammenhänge zwischen der Konfiguration und dem kritischen Volumenbruch beobachtet (3).

Um den Effekt bei Copolymeren zu studieren, wurde eine Reihe Polyester aus aliphatischen Dicarbonsäuren und Polyäthylenglykolen wech-

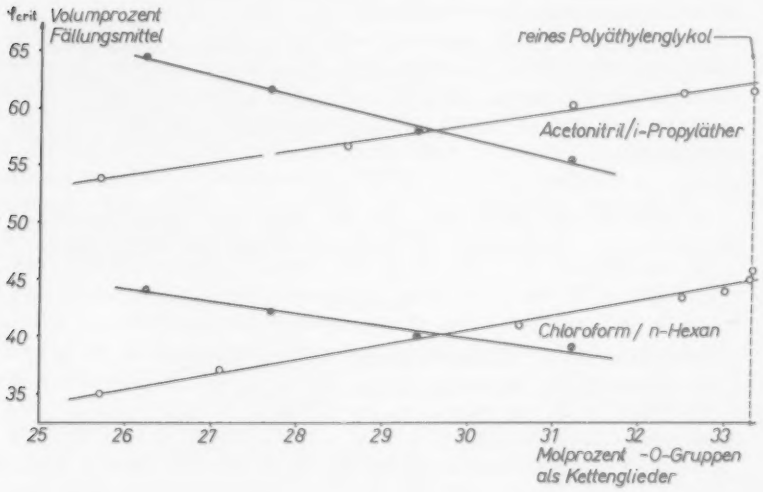

Abb. 1. Abhängigkeit des kritischen Volumbruches ψ_{crit} des Fällungsmittels vom Prozentgehalt an Sauerstoffgruppen an den insgesamt vorhandenen Kettengliedern für zwei Lösungsmittel/Fällungsmittel-Systeme für Polyester aus Adipinsäure und Polyäthylenglykolen verschiedenen Molekulargewichtes (o) und Polyester aus einem Polyäthylenglykol vom Molekulargewicht 400 und verschiedenen Dicarbonsäuren (●).

selnden Molekulargewichtes dargestellt. In einer ersten Versuchsreihe wurde Adipinsäure mit Polyäthylenglykolen mit Molekulargewichten zwischen 150 und 29 000 (Zahlenmittel) verestert, während in einer zweiten Versuchsreihe ein Polyäthylenglykol mit Molekulargewicht 400 mit einer der folgenden Dicarbonsäure umgesetzt wurde: Bernsteinsäure, Adipinsäure, Korksäure, Sebacinsäure. Als Lösungsmittel-/Fällungsmittel-Systeme wurden Chloroform/n-Hexan bzw. Acetonitril/i-Propyläther gewählt. Beim ersteren System scheidet sich bei Ueberschreiten des 1. Trübungspunktes z.B. reines Polyäthylenglykol vom Molekulargewicht 29 000 kristallin ab, während beim letzteren System im Bereich hoher Polymer-Konzentrationen eine Trennung in zwei flüssige Phasen auftritt. Die Trübungspunkt-Titrationen wurden in einer thermostatisierten und gerührten Zelle photoelektrisch verfolgt und mit einem x-y-Schreiber aufgezeichnet.

Wie man aus Abbildung 1 sieht, besteht in erster Näherung und innerhalb der experimentellen Fehlergrenzen eine lineare Beziehung zwischen dem kritischen Volumenbruch ψ_{crit} und dem prozentualen Anteil an Sauerstoffatomen als Kettenglieder. Kettenglieder sind $-CH_2-$, $-CO-$ und $-O-$. Die Methode sollte sich daher besonders zur Analyse von Copolymeren eignen, deren Grundbausteine sich in ihrer chemischen Zusammensetzung, ihrem Brechungsindex usw. nur wenig unterscheiden. Das Verfahren ist unabhängig vom Molekulargewicht der Polymeren, sofern $M \gtrsim 20\,000$. Da die Funktion linear ist, sind zur Eichung im Prinzip nur Messungen an den beiden Unipolymeren erforderlich. Experimentelle Einzelheiten, Messungen an anderen Systemen und die Ermittlung von relativen Solvatationsgraden werden in "Die Makromolekulare Chemie" veröffentlicht.

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SYNTHESIS OF POLY-m-XYLYLENE

The preparation of poly-p-xylylene and poly-o-xylylene has been described by a number of workers (1-10). We report the synthesis of poly-m-xylylene according to the Wurtz procedure, which has been shown effective in the preparation of unbranched crystalline poly-p-xylylene (9).

One equivalent of α, α'-dibromo-m-xylene dissolved in a small amount of freshly distilled dry dioxane was added with stirring, under nitrogen, to a suspension of four equivalents of finely divided metallic sodium in dry dioxane. The exothermic reaction was maintained at about 35°C. with an ice water bath. The reacting mixture turned dark blue and was kept at 35°C. for about two additional hours following exothermic reaction. The reaction mixture was then added dropwise, with vigorous stirring, into a tenfold excess of methyl alcohol and a light blue precipitate settled to the bottom. The clear liquid was decanted. The precipitate was washed several times with methanol, then with water, and repeatedly boiled in water. The blue color disappeared after initial boiling. The white polymer was then pulverized, the retained water extracted with methanol in a Waring Blendor, filtered, air dried, and finally dried under reduced pressure at 30°C. in a flow of nitrogen. 80% of the theoretical amount of material was obtained. Wide angle x-ray diffraction patterns indicated that the material was not crystalline. An ash content of less than 0.005% was found and no bromine was detected. Low molecular weight material was extracted with cold ether. The extracted polymer softened at 60°C., flowed freely at 190°C., and was insoluble in common solvents. The polymer evidenced IR absorption bands at 788 and 698 $cm.^{-1}$, characteristic of meta substituted aromatic rings.

Poly-o-xylylene was prepared in a similar way. The temperature during this polymerization was maintained between 17 and 20°C. After extracting low molecular weight material with cold ether the physical properties of the polymer were identical to the polymer prepared by an alternate synthesis (10).

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